Rearrangement of (Substituted benzyl)trimethylammonium Ylides in a Nonbasic Medium: The Improved Sommelet-Hauser Rearrangement

Mitsuji Nakano and Yoshiro Sato*

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan

Received August 6, 1986

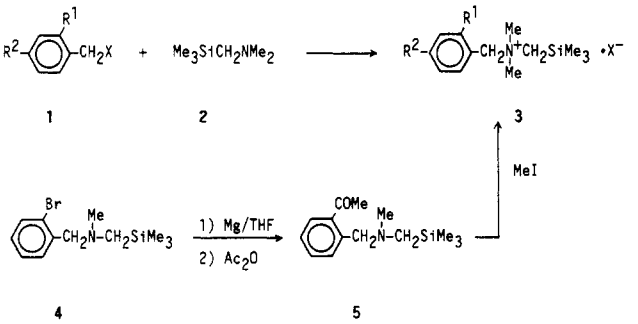
Benzyl quaternary ammonium ylide formation in a nonbasic medium was accomplished by fluoride anion induced desilylation of benzyldimethyl[(trimethylsilyl)methyl]ammonium bromide (**3a**) and ortho- or para-substituted benzyl analogues **3b-k**. Treatment of **3** with CsF in HMPA at room temperature gives high yields of the Sommelet-Hauser rearrangement products **7** from **3a** and methyl-, acetoxy- and chloro-substituted analogues **3b-f**. However, formation of the Stevens rearrangement products **8** is competitive for the reaction of compounds **3g-k** having strong electron-withdrawing substituents such as acetyl, cyano, and nitro groups. From the *o*-cyano-substituted analogue **3h**, a considerable amount of para Sommelet-Hauser rearrangement product is isolated.

The two base-promoted isomerizations of benzyl quaternary ammonium salts are well-known as the Stevens rearrangement and the Sommelet-Hauser rearrangement.[1] When structurally feasible, both rearrangements may occur simultaneously, thus limiting their synthetic utility, and their ratio is affected by the kinds of bases and solvents employed.[2] The only such reaction reported to give almost exclusively the Sommelet-Hauser rearrangement product involves treating benzyltrimethylammonium halides with sodium amide in liquid ammonia, and it provides a convenient synthetic route to *N,N*-dimethyl-2-methylbenzylamine.[3] However, this rearrangement does not occur if a substituent on the benzene ring prevents the formation of the required ylide intermediate. For example, halogen substituents decrease markedly the yield of rearrangement product, apparently because of benzyne formation.[4] Attempts to rearrange (*p*-cyanobenzyl)ammonium salts under these conditions have failed.[5]

It has been reported that the reaction of benzyldimethyl[(triorganosilyl)methyl]ammonium halides with lithium aluminum hydride or sodium amide involves cleavage of the carbon-silicon bonds to give ammonium ylide intermediates.[6] Vedejs et al. reported that [(trimethylsilyl)methyl]ammonium salts can be desilylated with fluoride anion and that the resulting intermediate undergo reactions characteristic of nitrogen ylide.[7] Accordingly, we have investigated the use of fluoride anion to cleave the Si-C bonds of benzyldimethyl[(trimethylsilyl)methyl]ammonium halides **3** in search of a new route to the Sommelet-Hauser rearrangement in a nonbasic medium.

Benzyldimethyl[(trimethylsilyl)methyl]ammonium halides **3a** and **3a'** and ortho- and para-substituted analogues **3b-f,h,i** were prepared by reaction of the corresponding benzyl halide derivatives **1** with [(dimethylamino)methyl]trimethylsilane (**2**). (2-Acetylbenzyl)dimethyl[(trimethylsilyl)methyl]ammonium iodide (**3g**) was

Scheme I



Scheme II

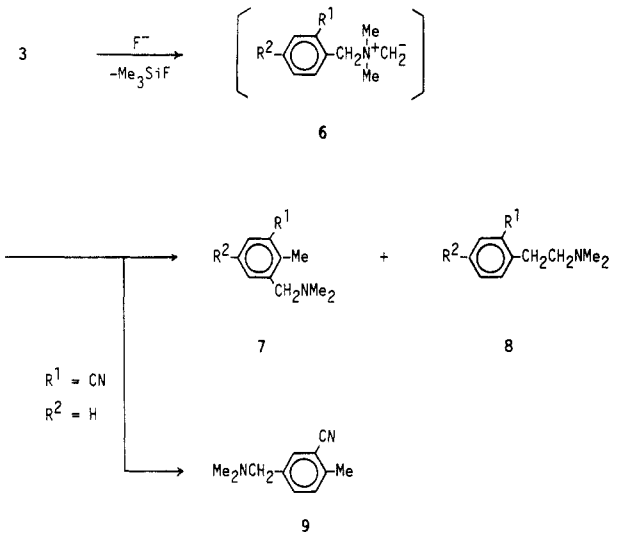


Table I. (Substituted benzyl)dimethyl[(trimethylsilyl)methyl]ammonium Halides 3

	R^1	R^2	X	yield from **2**, %
3a	H	H	Br	93
3a'	H	H	Cl	92
3b	Me	H	Br	92
3c	H	Me	Br	80
3d	H	OAc	Br	81
3e	Cl	H	Cl	90
3f	H	Cl	Cl	81
3g	COMe	H	I	90[a]
3h	CN	H	Br	83
3i	H	CN	Br	91
3j	NO_2	H	Br	*b*
3k	H	NO_2	Br	*b*

[a] Yield from **5**. [b] Not isolated.

(1) (a) Johnson, A. W. *Ylide Chemistry*; Academic: New York, 1966; Chapter 7. (b) Pine, S. H. *Organic Reactions*; Wiley: New York, 1970; Vol. 18, Chapter 4. (c) Lepley, A. R.; Giumanini, A. G. In *Mechanisms of Molecular Migrations*; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 3, p 297. (d) Kaiser, E. M.; Slocum, D. W. In *Organic Reactive Intermediates*; McManus, S. P., Ed.; Academic: New York, 1973; Chapter 5. (e) Zugravescu, I.; Petrovanu, M. *N-Ylid Chemistry*; McGraw-Hill: New York, 1976; Chapter 2.

(2) (a) Pine, S. H.; Munemo, E. M.; Fillips, T. R.; Bartolini, G.; Cotton, W. D.; Andrews, G. C. *J. Org. Chem.* **1971**, *36*, 984. (b) Bumgardner, C. L.; Hsu, H.-B.; Afghahi, F.; Robert, W. L.; Purrington, S. T. *J. Org. Chem.* **1979**, *44*, 2348.

(3) Brasen, W. R.; Hauser, C. R. *Organic Synthesis*; Wiley: New York, 1954; Vol. 34, p 61.

(4) Beard, W. Q., Jr.; Hauser, C. R. *J. Org. Chem.* **1960**, *25*, 334; **1961**, *26*, 371.

(5) Puterbaugh, W. H.; Hauser, C. R. *J. Am. Chem. Soc.* **1964**, *86*, 1108.

(6) (a) Sato, Y.; Sakakibara, H. *J. Organomet. Chem.* **1979**, *166*, 303. (b) Sato, Y.; Yagi, Y.; Kato, M. *J. Org. Chem.* **1980**, *45*, 613.

(7) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1979**, *101*, 6452.

0022-3263/87/1952-1844$01.50/0

Table II. Reaction of Benzyldimethyl[(trimethylsilyl)methyl]ammonium Bromide (3a) with the Fluoride Anion

entry	F^- source	solvent	reactn time, h	products (7 and 8) total yield, %	products (7 and 8) ratio[a] 7 to 8
1	TBAF	THF	38	61	97:3
2	TBAF	HMPA/THF (1:3)	17	74	98:2
3	CsF	HMPA	15	84	97:3
4	CsF	Me_2SO	15	54	99:1
5	CsF	Me_2SO/THF (1:2)	15	62	99:1
6	CsF	DMF	18	61	98:2
7	CsF	MeCN	15	tr	

[a] The ratio was determined by GLC analysis (10% PEG 20M).

Table III. Reaction of (Substituted benzyl)dimethyl[(trimethylsilyl)methyl]ammonium Halides 3 with Cesium Fluoride

entry		reactn time, h	products (7 and 8) bp,[a] °C (mmHg)	% yield[b] from 3	% yield[b] from 1	ratio[c] 7 to 8
1	**3a**	15	130 (150)	84	81	97:3
2	**3a′**	44		29		99:1
3	**3a′**	122		62		98:2
4	**3a′**	20[d]		75		99:1
5	**3b**	25	135 (155)	84		96:4
6	**3c**	25	135 (150)	77		96:4
7	**3d**	22	170 (20)	72		99:1
8	**3e**	25[d]	140 (105)	69		94:6
9	**3f**	23[d]	150 (160)	84		>99:<1
10	**3g**	24	130 (10)	54		42:58
11	**3h**	24	135 (17)	83		*e*
12	**3i**	25	140 (17)	88		81:19
13	**3j**	24	120 (20)		80	<1:>99
14	**3k**	24	130 (20)		77	12:88

[a] Oven temperature of a Buchi Kugelrohr distillation apparatus. [b] Total yield of 7 and 8. [c] The ratio was determined by GLC analysis (10% PEG 20M). [d] KI powder was added. [e] A mixture of three isomers (**7h**:**8h**:**9** = 25:59:16).

synthesized from *N*-methyl-*N*-[(trimethylsilyl)methyl]-2-bromobenzylamine (4) (Scheme I). The yields and characteristic data are shown in Tables I and IV.

When a suspension of **3a** in THF was treated with tetra-*n*-butylammonium fluoride (TBAF), desilylation proceeded slowly at room temperature to give the expected Sommelet–Hauser rearrangement product *N*,*N*-dimethyl-2-methylbenzylamine (**7a**) accompanied by a small amount of the Stevens rearrangement product *N*,*N*-dimethyl-2-phenylethylamine (**8a**). The reaction could be accelerated by addition of hexamethylphosphoramide (HMPA). However, the reaction products were contaminated with tri-*n*-butylamine from the TBAF reagent, and this impurity could not be separated from the reaction products by distillation because of their similar boiling points. We therefore investigated cesium fluoride as a source of fluoride ion in several solvents (Table II). Although the ratio of **7** to **8** was the same in all solvents tested, HMPA gave the best yield and was used in subsequent reactions.

When the counteranion was changed from bromide to chloride, the reaction rate decreased markedly, but this effect could be overcome by addition of an excess of KI powder (Table III, entries 1–4).

Since the reaction of **1** with **2** proceeds in quantitative yield, we investigated carrying out the quaternization and desilylation sequentially in the same flask. The reaction of **1** with **2** was carried out in THF; then, HMPA was added and the mixture was treated with CsF to give satisfactory yields of products (Table III, entries 1, 13, and 14).

When the substituent on the benzene ring was hydrogen, methyl, acetoxy, or chloro, the reaction was highly selective in giving the Sommelet–Hauser rearrangement products **7** (Table III, entries 1–9). Compounds with an acetyl or cyano substituent afforded mixtures of **7** and **8**, and those with a nitro group gave predominantly the Stevens products **8** (entries 10–14). Thus, the Sommelet–Hauser rearrangement products predominate from compounds substituted by electron-donating or weakly -withdrawing groups, and competing formation of the Stevens rearrangement products increases with an increase in the electron-withdrawing ability of the substituents. The ratio of Sommelet–Hauser to Stevens rearrangement products decreases for ortho- or para-substituted series in the order H > Me > OAc > Cl > Ac > CN > NO_2.

Three isomeric products were obtained from *o*-cyano compound **3h**: **7h**, **8h**, and the para Sommelet–Hauser rearrangement product *N*,*N*-dimethyl-3-cyano-4-methyl-

Table IV. (Substituted benzyl)dimethyl[(trimethylsilyl)methyl]ammonium Halides 3[a]

	mp, °C	NMR ($CDCl_3$) δ $SiCH_3$	NCH_3	$SiCH_2N$	NCH_2Ph	aromatic H	other
3a[b]	190–191	0.36	3.42	3.58	5.23	7.40–8.08	
3a′	209–210	0.36	3.42	3.58	5.22	7.40–8.08	
3b	190–191	0.31	3.40	3.67	5.15	7.21–7.59	2.60 ($PhCH_3$)
3c	175–176	0.30	3.07	3.53	5.15	7.34–7.76	2.42 ($PhCH_3$)
3d	193–194	0.30	3.37	3.49	5.21	7.26–7.94	2.35 (CH_3CO)
3e	167–169	0.34	3.43	3.64	5.22	7.38–7.61	
3f	194–195	0.29	3.42	3.50	5.32	7.47–7.91	
3g	135–136	0.50	3.30	3.70	5.45	7.42–8.30	2.73 (CH_3CO)
3h	160–162	0.40	3.47	3.72	5.31	7.63–8.58	
3i	191–193	0.33	3.47	3.57	5.54	7.97–8.33	

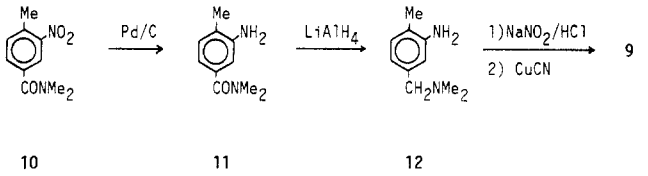
[a] Satisfactory analytical data (±0.3% for C, H, and N) were submitted for review. [b] Reference 6.

Table V. Substituted *N*,*N*-Dimethyl-2-phenylethylamines 8[a]

	^1H NMR ($CDCl_3$) δ NCH_3	NCH_2	$PhCH_2$	aromatic H	other
8g	2.32	2.42–2.67	2.95–3.19	7.19–7.75	2.59 (CH_3CO)
8h	2.30	2.87–3.11	2.49–2.71	7.14–7.78	
8i	2.30	2.43–3.10		7.42–7.68	
8j	2.28	2.42–2.68	2.76–3.00	7.20–7.92	
8k	2.28	2.44–2.68	2.76–3.00	7.36–8.08	

[a] Satisfactory analytical data or high-resolution mass spectra were submitted for review.

Scheme III



benzylamine (**9**), which was identical with an authentic sample synthesized independently (Scheme III). The normal Sommelet–Hauser ortho rearrangement is believed to involve concerted isomerization of an ylide to an *exo*-methylene intermediate that is the precursor of the final product **7**.[1] When the highly hindered amine (phenyl-*tert*-butylmethyl)trimethylammonium bromide was treated with base, Sommelet–Hauser rearrangement to the para position occurred in only a few percent yield.[2a] In the rearrangement of **3h**, the ratio of the ortho and para Sommelet-Hauser products (**7h** to **9**) is 61:39. The formation of such a high proportion of **9** indicates a mechanism involving an ion-pair or a radical-pair intermediate. The Stevens rearrangement proceeds by a radical-pair mechanism.[1] A radical dissociation–recombination mechanism may be involved in the formation of **9**.

Experimental Section

Hexamethylphosphoramide (HMPA) was dried by distillation under reduced pressure from sodium prior to use.[8] Tetrahydrofuran was distilled from sodium benzophenone ketyl. Cesium fluoride was dried over P_2O_5 at 180 °C under reduced pressure. A solution of tetra-*n*-butylammonium fluoride in THF was dried over molecular sieves (4A). NMR spectra were recorded on a JEOL JNM-PMX 60, MH-100, or FX-100 spectrometer with use of Me_4Si as internal standard. IR spectra were recorded on a Jasco IRA-2 spectrometer. Mass spectra were measured on a JEOL JMS-DX300 GC-MS system (70 eV). Gas chromatographic analyses were carried out on a Gasukuro Kogyo Model 370 chromatograph with flame ionization detector using a 2-m, 10% PEG 20M on Chromosorb AW column. All melting points and boiling points are uncorrected.

(Substituted benzyl)dimethyl[(trimethylsilyl)methyl]ammonium Halides (3a–f,h,i). A mixture of the appropriately substituted benzyl halide (**1a–f,h,i**; 8.6 mmol), [(dimethylamino)methyl]trimethylsilane (**2**; 7.5 mmol), and acetone (15 mL) was heated at reflux for 2 h. The precipitated crystals were filtered, washed with acetone, and dried. The yields and characteristic data are summarized in Tables I and IV.

***N*-Methyl-*N*-[(trimethylsilyl)methyl]-2-bromobenzylamine (4).** A solution of [(methylamino)methyl]trimethylsilane (4.13 g, 35.2 mmol) and 2-bromobenzyl bromide (6.75 g, 27 mmol) in acetone (30 mL) was heated at reflux for 3 days. The acetone was evaporated on a rotary evaporator, and the residue was taken up in AcOEt and 5% Na_2CO_3. The organic layer, after drying over $MgSO_4$, was concentrated, and the residue was distilled to give 4.23 g (55%) of **4**: bp 143–144 °C (15 mmHg); ^1H NMR ($CDCl_3$) δ 0.07 (9 H, s, $SiCH_3$), 2.00 (2 H, s, $SiCH_2$), 2.27 (3 H, s, NCH_3), 3.59 (2 H, s, $PhCH_2$), 7.14–7.77 (4 H, m, aromatic H). Anal. Calcd for $C_{12}H_{20}BrNSi$: C, 50.34; H, 7.04; N, 4.89. Found: C, 50.20; H, 6.92; N, 4.82.

***N*-Methyl-*N*-[(trimethylsilyl)methyl]-2-acetylbenzylamine (5).** A Grignard reagent, prepared from **4** (1.58 g, 5.53 mmol) and magnesium turnings (180 mg, 7.8 mmol) in THF (5 mL), was added slowly to a solution of acetic anhydride (847 mg, 8.3 mmol) in THF (5 mL) at −78 °C, and then the temperature was raised to room temperature. After the mixture was stirred for 5 h, 2% aqueous Na_2CO_3 (100 mL) was added and the mixture was extracted with ether. The ether layer was extracted with 10% HCl, the acid extract was neutralized with saturated aqueous Na_2CO_3, and then it was extracted with ether. The ethereal extract was dried ($MgSO_4$), concentrated, and distilled under reduced pressure: bp 110 °C (10 mmHg) (oven temperature of Kugelrohr). The distillate (492 mg) was chromatographed on a silica gel column (hexane:chloroform:triethylamine = 10:10:1) to give 375 mg (25%) of **5**: ^1H NMR ($CDCl_3$) δ 0.03 (9 H, s, $SiCH_3$), 1.93 (2 H, s, $SiCH_2$), 2.15 (3 H, s, NCH_3), 2.54 (3 H, s, $COCH_3$), 3.68 (2 H, s, $PhCH_2$), 7.23–7.63 (4 H, m, aromatic H). Anal. Calcd for $C_{14}H_{23}NOSi$: C, 67.32; H, 9.29; N, 5.62. Found: C, 66.92; H, 9.30; N, 5.80.

(2-Acetylbenzyl)dimethyl[(trimethylsilyl)methyl]ammonium Iodide (3g). A solution of **5** (375 mg, 1.5 mmol) and methyl iodide (319 mg, 2.25 mmol) in acetone (8 mL) was heated at reflux for 48 h. After evaporation of the solvent, the residue was crystallized from a mixture of ether and acetone to give 530 mg (90%) of **3g**. Melting point and spectral data are shown in Table IV.

Reaction of (Substituted benzyl)dimethyl[(trimethylsilyl)methyl]ammonium Halides 3a–f with CsF. General Procedure. In a 20-mL flask equipped with a magnetic stirrer and a dropping funnel was placed the ammonium halide (2 mmol), CsF (1.5 g, 10 mmol), and KI powder (1 g, 6 mmol) when the chloride (**3a′**, **3e**, **3f**) was employed. The flask was dried under reduced pressure, and was flashed with high-purity nitrogen. HMPA (10 mL) was added into the flask, and the mixture was stirred at room temperature (see Table III). The mixture was mixed with 2% Na_2CO_3 (200 mL) and was extracted with ether (100 mL × 4). The ethereal extract was washed with 1% Na_2CO_3 (100 mL × 2), dried over $MgSO_4$, and concentrated. Kugelrohr distillation of the residual oil gave a mixture of two isomers (**7**, **8**), and the ratio was determined by GLC analysis (see Table III). Their structures were confirmed by ^1H NMR, ^{13}C NMR, GC–MS, and IR spectra.

Compounds **7** showed ^1H NMR peaks in $CDCl_3$ at δ 2.23–2.29 (NCH_3), 2.33–2.57 ($PhCH_3$), and 3.37–3.44 ($PhCH_2N$); additional peaks were seen in **7b**[9] (δ 2.27, $PhCH_3$), **7c**[4] (δ 2.33, $PhCH_3$), **7d** (δ 2.29, CH_3CO), and **7g** (δ 2.54, CH_3CO).

The yields and other characteristic data are summarized in Tables III and V.

Reaction of (2-Acetylbenzyl)dimethyl[(trimethylsilyl)methyl]ammonium Iodide (3g) with CsF. In a manner similar to that described in the general procedure, **3g** (391 mg, 1 mmol), CsF (750 mg, 5 mmol), and HMPA (5 mL) were treated to give 103 mg (54%) of a mixture of **7g** and **8g**: bp 130 °C (10 mmHg) (Kugelrohr). The mixture was chromatographed on a silica gel column (chloroform:triethylamine = 10:1) to give **7g** (31 mg) and **8g** (42 mg).

Reaction of (2-Cyanobenzyl)dimethyl[(trimethylsilyl)methyl]ammonium Bromide (3h) with CsF. In a manner as described for **3a–f**, **3h** (655 mg, 2 mmol) and CsF (1.5 g, 10 mmol) in HMPA (10 mL) were treated to give 286 mg (83%) of a mixture of three isomers (**7h**, **8h**, **9**): bp 135 °C (17 mmHg). The mixture was chromatographed on a silica gel column (chloroform bubbled with ammonia gas) to give *N*,*N*-dimethyl-2-methyl-3-cyanobenzylamine (**7h**; 66 mg), *N*,*N*-dimethyl-2-(2-cyanophenyl)ethylamine (**8h**; 147 mg), and *N*,*N*-dimethyl-3-cyano-4-methylbenzylamine (**9**; 45 mg). The ratio of the three isomers in the distillate was determined on a Merck Kieselgel 60 F_{254} plate with Shimazu dual-wavelength TLC scanner CS-900 at 254-nm UV; **7h**:**8h**:**9** = 25:59:16.

9: ^1H NMR ($CDCl_3$) δ 2.23 (6 H, s, NCH_3), 2.52 (3 H, s, $PhCH_3$), 3.40 (2 H, s, CH_2), 7.26 (1 H, d, J = 8 Hz), 7.42 (1 H, dd, J = 8 and 2 Hz), 7.54 (1 H, d, J = 2 Hz); ^{13}C NMR ($CDCl_3$) δ 20.1 (q), 45.3 (q), 63.1 (t), 112.7 (s), 118.1 (s), 130.2 (d), 132.7 (d), 133.3 (d), 137.5 (s), 140.6 (s); IR (film) 2220 cm^{-1}. Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.60; H, 8.27; N, 15.89.

Reaction of (4-Cyanobenzyl)dimethyl[(trimethylsilyl)methyl]ammonium Bromide (3i) with CsF. In a manner as described for **3a–f**, **3i** (655 mg, 2 mmol) and CsF (1.5 g, 10 mmol) were treated to give 306 mg (88%) of a mixture of **7i** and **8i**: bp 140 °C (17 mmHg). The mixture was chromatographed on a silica gel column (chloroform:MeOH = 15:1, bubbled with ammonia gas) to give **7i** (170 mg) and **8i** (40 mg).

Reaction of (2-Nitrobenzyl)dimethyl[(trimethylsilyl)methyl]ammonium Bromide (3j) with CsF. A mixture of

(8) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1980; p 282.

(9) Kantor, S. W.; Hauser, C. R. *J. Am. Chem. Soc.* **1951**, *73*, 4122.

2-nitrobenzyl bromide (**1j**; 432 mg, 2 mmol), **2** (315 mg, 2.4 mmol), and THF (5 mL) was heated at 50 °C for 2 h. Then, HMPA (10 mL) and CsF (1.5 g, 10 mmol) were added and the mixture was stirred for 24 h at room temperature. The reaction mixture was mixed with 2% Na_2CO_3 (200 mL) and extracted with ether (100 mL × 4). The ethereal extract was washed with water (100 mL × 2), dried ($MgSO_4$), and concentrated. Distillation of the residue gave 311 mg (80%) of **8j**. The spectral data are summarized in Table V.

Reaction of (4-Nitrobenzyl)dimethyl[(trimethylsilyl)methyl]ammonium Bromide (3k) with CsF. In a manner similar to that described for **3j**, 4-nitrobenzyl bromide (**1k**; 432 mg, 2 mmol), **2** (315 mg, 2.4 mmol), and CsF (1.5 g, 10 mmol) were allowed to react to give 299 mg (77%) of a mixture of **7k** and **8k**: bp 130 °C (20 mmHg). A part of the mixture (244 mg) was separated on a silica gel column (ether:triethylamine = 20:1) to give **7k** (23 mg) and **8k** (172 mg).

***N,N*-Dimethyl-3-amino-4-methylbenzamide (11).** A mixture of *N,N*-dimethyl-3-nitro-4-methylbenzamide[10] (20.82 g, 0.1 mol) and 5% Pd/C (950 mg) in EtOH (200 mL) was shaken with hydrogen until no more hydrogen was absorbed. The catalyst was filtered off, and the filtrate was concentrated. The residue was taken up in chloroform and 10% HCl. The acidic layer was neutralized with aqueous Na_2CO_3 and extracted with chloroform. The extract was dried over $MgSO_4$ and concentrated, and the residue was recrystallized from hexane to give 15.65 g (88%) of **11**: mp 98–99 °C; ^1H NMR ($CDCl_3$) δ 2.16 (3 H, s, $PhCH_3$), 3.05 (6 H, s, NCH_3), 3.75 (2 H, s, NH), 6.77 (1 H, dd, J = 8 and 2 Hz), 6.82 (1 H, d, J = 2 Hz), 7.11 (1 H, d, J = 8 Hz, aromatic H); IR (Nujol) 3320, 3400 (NH), 1650 (CO) cm^{-1}. Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.39; H, 7.92; N, 15.71.

***N,N*-Dimethyl-3-amino-4-methylbenzylamine (12).** A mixture of **11** (3.57 g, 20 mmol), $LiAlH_4$ (1.14 g, 30 mmol), and THF (60 mL) was stirred for 48 h at room temperature. The mixture was treated with AcOEt (1 mL) and 10% NaOH (4 mL) and then was filtered. The filtrate and washings of the precipitate were dried ($MgSO_4$) and concentrated. The residue was recrystallized from hexane to give 2.38 g (72%) of **12**: mp 73–76 °C; ^1H NMR ($CDCl_3$) δ 2.15 (3 H, s), 2.24 (6 H, s), 3.35 (2 H, s), 3.66 (2 H, br s), 6.72 (1 H, dd, J = 8 and 2 Hz), 6.75 (1 H, d, J = 2 Hz), 7.06 (1 H, d, J = 8). Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.13; H, 9.82; N, 17.06. Found: C, 73.02; H, 9.64; N, 16.92.

***N,N*-Dimethyl-3-cyano-4-methylbenzylamine (9).** To an ice-cooled mixture of **12** (821 mg, 5 mmol), 35% HCl (1.5 mL), and water (5 mL) was added dropwise a solution of $NaNO_2$ (345 mg, 5 mmol) in water (2 mL), and stirring was continued for 2 h. The mixture was neutralized to pH 7 with aqueous Na_2CO_3, and then it was added to an ice-cooled suspension of CuCN (896 mg, 10 mmol) in water (6 mL). After 2 h of stirring, the reaction mixture was made basic with aqueous Na_2CO_3 and extracted with ether. The ether layer was extracted with 10% HCl. The acidic extract was neutralized, and then it was extracted with ether. The ethereal extract was dried ($MgSO_4$) and concentrated. Distillation of the residue gave 261 mg of a colorless oil [bp 135 °C (17 mmHg)], which was chromatographed on a preparative TLC (Merck, Kieselgel 60 F_{254}, AcOEt bubbled with NH_3 gas). A separated oil (61 mg) was distilled to give 39 mg (5%) of **9**, bp 100 °C (17 mmHg) (Kugelrohr). The spectral data showed good agreement with that of the sample isolated from the reaction mixture of **3h** with CsF.

(10) Scherpenzeel, V. *Recl. Trav. Chim. Pays-Bas* **1901**, *20*, 159.

Ring-Opening Rearrangements of Sesquinorbornyl Cations

Paul D. Bartlett,* Michael D. Ravenscroft, and Antonius A. M. Roof

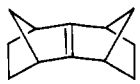
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Received September 25, 1986

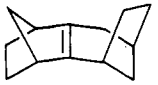
In superacid media, *anti*-sesquinorbornene (**2**) is protonated to yield the directly related carbocation 2^+ at −78 °C. On raising the temperature the cation rearranges irreversibly with ring opening to the 1-(2-norbornyl)-2-cyclopentenyl allylic cation 3^+. This rearrangement does not occur with *syn*-sesquinorbornene, within the temperature range studied, but is observed in the syn isomer **7** whose double bond is not shared between the norbornene ring systems. These observations permit the formulation of a general mechanism for the formation of the allylic cation.

Introduction

Of the five isomeric octahydro-1,4,5,8-dimethanonaphthalenes, the name "sesquinorbornenes" has been applied to those two isomers in which the norbornene units share a common double bond: *syn*- (**1**, SSNB)[1] and *anti*-sesquinorbornene (**2**, ASNB).[2] These two molecules possess some interesting structural and chemical features.[3,4]



SSNB (1)



ASNB (2)

Table I. ^{13}C NMR Chemical Shifts[a] for 2^+ at −75 °C and for the Species 3^+ Obtained at −25 °C

2^+	3^+	2^+	3^+
312.9 (s)	266.8 (s)	44.7 (t)	45.1 (t)
76.0 (d)	219.9 (d)	40.7 (t)	40.8 (t)
69.8 (d)	145.1 (d)	33.8 (d)	37.4 (d)
55.7 (d)	56.5 (d)	27.8 (t)	37.3 (t)
53.6 (d)	47.6 (t)	23.1 (t)	30.4 (t)
48.9 (t)	46.5 (d)	20.8 (t)	27.4 (t)

[a] ppm, CD_2Cl_2 (at 53.1 ppm) as internal standard.

X-ray crystallographic studies on ASNB[7] and on derivatives of SSNB[5a] show a planar double bond for the former

(1) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186, 7218.

(2) Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383.

(3) (a) Bartlett, P. D.; Roof, A. A. M.; Winter, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6520. (b) Roof, A. A. M.; Winter, W. J.; Bartlett, P. D. *J. Org. Chem.* **1985**, *50*, 4093. (c) Paquette, L. A. In *Stereochemistry and Reactivity of Systems Containing π-electrons*; Watson, W. H., Ed.; Verlag Chemie: Gainesville, FL, 1983; Chapter 2.

(4) (a) Gleiter, R.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, *23*, 927. (b) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron* **1983**, *39*, 3345. (c) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980. (d) Johnson, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1135. (e) Jørgensen, F. S. *Tetrahedron Lett.* **1983**, *24*, 5289.

(5) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022. (b) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553. (c) Paquette, L. A.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Org. Chem.* **1983**, *48*, 1250.

0022-3263/87/1952-1847$01.50/0